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A study of the evaporation rates of small freely falling water droplets

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A STUDY OF THE EVAPORATION RATES OF SMALL FREELY FALLING WATER DROPLETS

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ABSTRACT

The evaporation rates of small (radius 3-9μ), freely falling water droplets were determined. The droplets, produced in a diffusion cloud chamber, were allowed to fall through air of known relative humidity (95-100%) and at three ambient temperatures (25C, 30C, and 35C) in a vertical drift tube. The rates of evaporation were ascertained by recording the drop positions on film at fixed time intervals. The results are compared with several existing theories, and are found to lie between the formulation of Kinzer and Gunn, and the quasistationary theory based on Maxwell's equation.

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INTRODUCTION

It is a well known fact that surface properties are different from those of the corresponding bulk phases, and that in any heterogeneous phenomenon, surface properties are at least as important as bulk properties. Therefore, anything that can have an effect on a surface is of importance. One phenomenon of interest to the Atmospheric Sciences is the behavior of cloud-size water droplets, of radii up to approximately 10 microns. One specific aspect of this phenomenon is evaporation, a heterogeneous process. In the atmosphere are many trace impurities that may have an effect on the surface properties of water, and thus on the evaporation of the droplets.

An investigation has been initiated to determine the effects of surface active materials on the evaporation rates of water droplets. However, in order to determine these effects, the rates of evaporation of pure water droplets must be known. Unfortunately there is a paucity of data avialable for the rates of evaporation of small, ventilated (or freely falling) water droplets.

The present investigation is an attempt to acquire the necessary data, and at the same time, to compare the observed results with various theoretical formulations.

BACKGROUND

Many models of varying complexity have been proposed for the theory of droplet growth and evaporation, and can roughly be divided into two major types: diffusion theory, and kinetic theory.

Kinetic theory is most applicable to problems in which the drop radius is of the same order of magnitude, or less than the mean free path, ventilation and turbulence factors are large, or when dealing with evaporation through monolayers (Zung and Okuyama, 1965). Where the above factors are not involved, diffusion theory has proven to be successful in describing the evaporation of droplets, and this has been the area of major emphasis. Since the present problem does not involve those aspects for which kinetic theory would be more applicable, the background material to be presented will be primarily concerned with diffusion theory.

NONVENTILATED DROPS

Diffusion theory, as a description of drop evaporation, was proposed by Maxwell in 1877 (Fuchs, 1959), and this constituted a basis for diffusion theories that followed. Maxwell's model for drop evaporation, or stationary state evaporation, assumed that the rate of evaporation was solely dependent on the rate at which evaporating molecules diffused through the surrounding gaseous media. Also, he assumed that

the drop was spherical and at rest with respect to the surrounding medium, the vapor concentration at the surface of the drop was equal to the saturation concentration corresponding to the temperature of the drop surface, and that the evaporation was a steady state equilibrium process.

Starting with Fick's second law of diffusion expressed in spherical coordinates:

$$\frac{\partial(cr)}{\partial t} = D\frac{\partial^2(cr)}{\partial r^2} \quad , \tag{1}$$

where c is the vapor concentration, r is the radial coordinate, and D is the constant diffusion coefficient. For stationary evaporation

$$\frac{\partial(cr)}{\partial t} = 0 \quad . \tag{2}$$

Upon integrating the right hand side of Eq. 1, and making use of the boundary conditions:

$$c(r=a) = c_s \text{ and } c(r=\infty) = c_\infty \quad ,$$

where a is the drop radius, one obtains:

$$c = c_\infty + \frac{a}{r}(c_s - c_\infty) \quad . \tag{3}$$

Since the evaporation is stationary, the rate of diffusion, I, of the vapor is constant across any spherical surface of

radius r, concentric with the center of the drop. Expressed as Fick's first law,

$$I = -4\pi r^2 D\frac{\partial c}{\partial r} , \tag{4}$$

or if the surface of the drop is chosen for the surface in question,

$$I = -4\pi a^2 D\frac{\partial c}{\partial r}\Big|_{r=a} . \tag{5}$$

Taking the partial derivative of Eq. 3 with respect to r and substituting the result into Eq. 5, one obtains what is known as Maxwell's equation for the evaporation of a drop,

$$I = 4\pi aD(c_s - c_\infty) = I_M . \tag{6}$$

When I is given as dm/dt, where m is the mass of the spherical drop, Maxwell's equation can be written as:

$$\frac{d(a^2)}{dt} = \frac{2D}{\rho_\ell}(c_s - c_\infty) , \tag{7}$$

where ρ_ℓ is the density of the drop.

If it is assumed that the vapor obeys the ideal gas law, c = pM/RT, where p is the vapor pressure of the evaporating substance, M is the molecular weight, R is the gas constant, and T is the absolute temperature, then Eq. 6 may be written:

$$I_M = 4\pi a \frac{DM}{RT}(p_s - p_\infty) \quad . \qquad (8)$$

Langmuir (1918) derived an equation of this form for evaporation into a vacuum, with $p_\infty = 0$.

Houghton (1933) experimentally determined the rates of evaporation of water drops, 25 to 2600 micron in diameter, that were suspended from fine wires or glass filaments. His results, with approximate corrections made for the cooling of the drop, showed a linear relationship between the concentration difference $c_s - c_\infty$ and the surface of the sphere rate of evaporation, and were in "general agreement with the theoretical evaporation equation" (ibid). It is noted that the equation that Houghton used was derived by making an analogy to electrostatics, and was equivalent to Maxwell's equation. When Houghton first plotted his data, he found that $d(a^2)/dt$ was not linear with respect to $\rho_s - \rho_\infty$, where the vapor density was used as a measure of the concentration c. ρ_s is the water vapor density corresponding to saturation at the temperature of the drop and ρ_∞ is that corresponding to the humidity present in the surrounding air. The drop temperature was initially assumed to be at the ambient temperature.

Houghton's explanation for the discrepancy was that the drops had cooled to a temperature lower than the ambient temperature because of the evaporation process. Houghton attempted to arrive at a psychrometric equation for

evaporating drops, the results of which were used to compute corrected drop temperatures. It was with the corrected temperatures that his data showed the linear relationship. However, Houghton found that the diffusion coefficient obtained from his results was appreciably lower than that given in the International Critical Tables.

As pointed out by Fuchs (1959), the psychrometric equation used by Houghton was, in part, the reason for the discrepancy, as it did not take into account the heat flow to the drop through the support. Fuchs (1934) also recalculated D using a geometric mean, $(D_s D_\infty)^{\frac{1}{2}}$ and Houghton's data for low humidity (0-42%). The subscripts s and ∞ refer to the value of D at the temperature of the drop, and at the temperature of the surrounding media. Fuchs found that the diffusion coefficient thus obtained agreed to within a few percent with accepted values. For air at moderately low humidity, Houghton's values of D were widely scattered, which was possibly due to measurement errors in the determination of the humidity (Fuchs, 1934).

Besides the verification of Maxwell's equation, Houghton's work is also noteworthy because of his recognition of the fact that the evaporation process had lowered the temperature of the droplets. Although Fuchs (1934, 1959) points out other reasons for the discrepancies in Houghton's results, Houghton's point is well taken as the effect of evaporation on the drop temperature, and the correction to Maxwell's equation for this effect is quite important,

especially for volatile liquids.

Whereas Maxwell was only concerned with mass diffusion, in reality, the evaporation process involves not only mass transfer, but also heat flow. Therefore, when solving the drop evaporation problem, both the mass diffusion and heat flow problems have to be solved simultaneously. This was done by Fuchs (1934). In his model, he assumed that heat transfer was solely due to conduction, and the radiation and convection aspects were neglected. Also, he assumed that the coefficient of thermal conductivity, κ, was constant throughout the surrounding gas. Then, for stationary state conditions it follows that the temperature should follow laws analogous to those for mass diffusion. In other words for

$$\frac{\partial^2 T}{\partial r^2} = 0 \ , \tag{9}$$

the solution is given by

$$T = \frac{a}{r}(T_a - T_\infty) + T_\infty \ , \tag{10}$$

where T_a is the temperature of the drop surface, and T_∞ is the temperature of the gas at an infinite distance.

For stationary state evaporation the equilibrium conditions require that the heat used in evaporation be equal to the heat flux to the drop from the surrounding gas. In mathematical terms:

$$DL\frac{\partial c}{\partial r}\Big|_{r=a} = -\kappa\frac{\partial T}{\partial r}\Big|_{r=a} , \qquad (11)$$

where L is the latent heat of vaporization. Obtaining the partial derivatives from Eqs. 9 and 10, Eq. 11 becomes

$$T_\infty - T_a = \frac{1}{\Gamma}(c_s - c_\infty) , \qquad (12)$$

where $\Gamma=\frac{\kappa}{DL}$. Assuming the vapor obeys the ideal gas law, Eq.12 can be rewritten:

$$T_\infty - T_a = \frac{M}{R\Gamma}(p_a/T_a - p_\infty/T_\infty) . \qquad (13)$$

It is noted at this point that the vapor pressure is a function of the temperature. For small differences in temperature, the Clausius-Clapeyron equation, integrated for an ideal gas, can be used for the needed relationship. The rate law then has the form (Fuchs, 1934)

$$I = I_M\left(1 - \frac{Lc_\infty}{\Gamma R T_\infty^2}\right) . \qquad (14)$$

Fuchs (1959) lists those experiments in which large drops were hung from wires or glass filaments, and where an attempt was made to measure the drop temperature. In most cases it is noted (ibid) that the heat flow into the drop due to the presence of the support was not adequately compensated for, and the measured temperature differed

greatly from the calculated temperature. Fuchs does mention the work of Ranz and Marshall (1952) in which the temperature of drops was measured by 0.5 mil thermocouples. The droplets had diameters ranging from 0.06 to 0.11 cm and were supported by fine glass capillaries. Their results indicated that the true temperature of the drop can be measured.

There are many other corrections that can be made to the Maxwell rate. Two of the more often mentioned are noted below. The first of these involves the effect of a curved surface on the vapor pressure of a droplet. The Kelvin equation gives:

$$\frac{p_r - p_\infty}{p_\infty} = \frac{c_r - c_\infty}{c_\infty} = \frac{2\sigma M}{\rho_\ell r R T} , \qquad (15)$$

where the subscripts r and ∞ refer to a curved surface of radius r and a flat surface respectively, σ is the surface tension and ρ_ℓ is the density of the drop. This correction becomes important as the drop radius becomes small.

The second correction involves the possible effect of absorbing walls on the rate of evaporation. This problem has been investigated by Bradley, Evans and Whytlaw-Gray (1946), Luchak and Langstroth (1950), and Fuchs (1934). Their correction terms differ, but all show that a correction term for absorbing walls is important when the dimensions of the enclosing vessel are of the same order of magnitude as that of the drop.

It is best to note at this point that, whereas the

development of an evaporating droplet model presented so far has been for stationary evaporation, in reality, the evaporation of a droplet is a nonstationary process with a changing rate, and the evaporating surface is continually decreasing. The mathematics can become quite complicated in trying to completely solve the nonstationary evaporation problem. Because of this Fuchs, and those that followed his lead, fell back on a quasistationary model. The quasistationary model assumes that at any given instant, the rate of evaporation is the same as in the stationary state whose boundary conditions correspond to those of the nonstationary state at the instant of time in question. It is also assumed that the time required for the nonstationary process to become stationary is quite small compared to the lifetime of the drop.

To show the validity of the quasistationary model, Fuchs (1934, 1959) studied the problem of nonstationary evaporation. He first solved the problem of a stationary drop evaporating into an infinite media with initial vapor concentration c_∞. The decrease in temperature of the drop was ignored. The problem involves the solution of

$$\frac{\partial(cr)}{\partial t} = D\frac{\partial^2(cr)}{\partial r^2} ,$$

with the boundary conditions: $c=c_\infty$ at $t=0$ and $r>a$, and $c=c_o$ at $t>0$ and $r=a$. The solution to the problem gives the rate of evaporation as:

$$I = I_M\left(1 + \frac{a}{\sqrt{\pi Dt}}\right) . \qquad (16)$$

Even for a heavy fog or drizzle droplet (a=100μ), the correction to the stationary rate amounts to approximately 1% after one second.

It is convenient to know to what extent the evaporation process can be considered stationary. This can be done by comparing the time t_1 that it takes the term $\sqrt{\pi Dt}$ to reach a definite small value, Δ, with the lifetime, t_2, of the drop. For a given Δ of 0.01, and a water drop evaporating into dry air at 21.7C, t_1/t_2=0.043. In other words, the nonstationary rate exceeds the stationary rate by only 1% after approximately 1/20th of the time of the total evaporation has passed. For air that has water vapor already present in it, or for less volatile liquids, the approximation to the stationary state is more quickly reached.

An objection to the above formulation is the use of the infinite boundary condition. In this case, an infinite amount of water vapor must be imparted to the system by the drop during the transient period. However, one can still show that the evaporation process is for the most part approximated by a stationary state. This is done by choosing a finite distance for the outer boundary, but one that can be considered "infinite" with respect to the drop radius. If, for example, the outer boundary is chosen as 10^{-2} cm for a 5 micron drop evaporating into air with a relative humidity greater than

95%, the mass of water vapor imparted to the system during the transient period is 10^{-4} times that of the drop. For this case the evaporation during the transient period has had but a small effect on the total mass of the drop.

Fuchs also investigated the problem involved with the diminishing drop size, and his conclusions again were that the quasistationary assumptions were a good approximation for the evaporation of water droplets.

The effect of the change in radius on the evaporation rate was also studied by Luchack and Langstroth (1950) for the case of a droplet evaporating in a spherical vessel with absorbing walls.

Objections have been raised concerning the validity of the quasistationary model. Kirkaldy (1958) studied the problem of time-dependent diffusion theory, and arrived at a rate law identical to that given by the quasistationary model. He stated, however, that this agreement should not be used as a justification for the quasistationary calculation, as the mathematical procedure used for the quasistationary model was questionable. It is Kirkaldy's opinion that the evaporation phenomenon will not have an acceptable theoretical description until the theory is derived without any reference to stationary states.

Philip (1965) also studied the nonstationary problem, but in a more general form. The solution for the case of droplet evaporation can be found in Carslaw and Jaeger (1959) as well as the nonstationary evaporation problem in which

the radius is held constant. Philip, using a perturbation method, arrived at an approximate expression for the case in which the radius changes. He also states that, even with the shortcomings in the mathematical procedure used, and other objections, the quasistationary model is sufficient for most meterological purposes.

Another important refinement to the Maxwell rate of evaporation concerns the change in the vapor concentration at the surface of an evaporating drop. It was known to the early investigators that a temperature gradient abruptly rises as it approaches a surface at a temperature different from that of the surrounding media, beginning at a distance from the surface comparable to the mean free path, λ, of the air molecules. Since the laws governing mass diffusion and temperature conductivity are analogous, this gave them reason to believe that there was a change in the gradient of vapor concentration at the surface of an evaporating drop. The idea of the concentration jump distance was first proposed by Fuchs (1934). He assumed that Fick's law was only applicable up to a distance Δ, of the same order of magnitude as λ, from the drop, and that between the drop surface and the distance Δ away, the rate of evaporation was that for in a vacuum. The resultant rate of evaporation as given by Fuchs is

$$I = I_M\left(\frac{D}{rv\alpha} + \frac{r}{r+\Delta}\right)^{-1}, \qquad (17)$$

where $v=(kT/2\pi m)^{-\frac{1}{2}}$ and α is the evaporation-condensation coefficient. As noted by Bradley (1946), Fuchs' evaluation of Δ was left in an indefinite form. Bradley derived the expression:

$$\Delta = \lambda_2 \left(\frac{m_1+m_2}{m_1}\right)^{\frac{1}{2}} \tag{18}$$

for the value of Δ, where m_1 and m_2 refer to the mass of the air and evaporating molecules respectively. Bradley's experimental results on the evaporation of dibutyl phthalate and butyl stearate drops at various vapor pressures supported Fuchs' equation for the rate of evaporation.

Some other investigators who have derived similar rate laws, or who have investigated discontinuities at the drop surface are Tsuji (1950), Monchik and Reiss (1954), Wright (1960, 1961-1962), Brock (1964), Okuyama and Zung (1967), and Carstens and Kassner (1968). The paper by Okuyama and Zung was primarily concerned with the calculation of the evaporation-condensation coefficient, but includes a comparison of the rate equations given by Maxwell, Fuchs, and Monchick and Reiss. The work by Carstens and Kassner was concerned with obtaining a "connection" between kinetic and diffusion theory for the growth of droplets of sizes from 10^{-6} to 10^{-3} cm in radius. The "connection" was achieved by equating the flux expressions for each regime. In this manner, both the heat flow and diffusion problems were incorporated into the theory, which sets the work apart from

many of the other formulations derived for drop growth or evaporation for drop sizes of the same order of magnitude as the mean free path.

Experiments to determine the rates of evaporation of nonventilated drops can be classified in two categories; those that involve evaporating drops that were supported, and those that involve free drops. It is seen that both methods have their limitations. The smallness of a supported drop is dependent on the size of support available. Also, the interpretation of the data is complicated by the corrections that have to be made for heat flow along the support, and the distortion of the drop's shape by the support. On the other hand, while the above considerations are eliminated for a free drop, the drop size is limited to less than a 5 micron radius. This is because, for most cases, experiments using free drops have been performed in a Millikan type apparatus, and the electric fields used would not support larger drops. Also, with smaller drops convection currents and Brownian movement make accurate measurements much harder to obtain.

In general for the ranges of drop radius mentioned above, experimental results have tended to verify the Fuchs or Tsuji- Monchik and Reiss laws. Zung and Snead (1967) have given a fairly complete bibliography of the work done.

Two experiments are worth mentioning as their results have been an exception to the rule. The first, by Gudris and Kulikova (1924), was a study on the evaporation rate of

water droplets of 0.1 to 1.0 micron radius. They found that the evaporation rates were on the order of 10^{-13} cm^2/sec, or 10^5 times slower than the rates given by the quasistationary theory. In the second, Gokhale (1963), in a like manner, studied water droplets of approximately 1 micron radius, and found that the evaporation rates agreed with the results of Gudris and Kulikova. Snead and Zung (1968), however, found qualitatively that water droplets with radii in the range studied above evaporated considerably faster than 10^{-8} cm^2 per sec. It is their comment concerning the results of Gudris and Kulikova, and Gokhale, that it was likely that the conditions under which the drops evaporated were those of air saturated with water vapor, or nearly so.

VENTILATED DROPS

When dealing with mass or heat transfer in a moving media, it is often convenient to use dimensionless numbers. Some of the most common are noted below.

$$\text{Reynolds number: } Re = \frac{2Va}{\nu} , \tag{19}$$

where V is the velocity of the stream with respect to the sphere of radius a at a distance removed from the sphere, and $\nu=\frac{\eta}{\rho}$ is the kinematic viscostiy of the medium, where η is the viscosity and ρ is the density of the medium.

$$\text{Nusselt Number: } Nu = \frac{2rQ}{\kappa S(T_\infty - T_o)} , \tag{20}$$

where Q is the amount of heat transferred to the body by the medium per unit time, S is the surface area of the body, κ is the thermal conductivity of the medium, and $T_\infty - T_o$ is the difference in temperature between the medium and the body.

$$\text{Sherwood number: } Sh = \frac{2rI}{DS(c_o - c_\infty)} , \tag{21}$$

where I is the rate of weight loss of the body and D is the diffusion coefficient.

$$\text{Prandtl number: } Pr = \nu/\chi , \tag{22}$$

where $\chi = \frac{\kappa}{\gamma_g C_p}$ is the temperature conductivity of the medium.

$$\text{Schmidt number: } Sc = \nu/D . \tag{23}$$

The problem of an evaporating drop moving with respect to a medium is quite complicated, as not only is diffusion involved, but also fluid mechanics. That part of the problem concerning fluid mechanics can be described by the Navier-Stokes equation, written here in psuedo-vectorial form (Sommerfeld, 1964),

$$\rho\frac{\partial \underset{\sim}{V}}{\partial t} + \rho(\underset{\sim}{V}\,\mathbf{grad}\,\underset{\sim}{V}) - \eta\nabla^2\underset{\sim}{V} + \text{grad } P = \underset{\sim}{F} , \tag{24}$$

where ρ is the density of the medium, $\underset{\sim}{V}$ is the velocity of the flow, η is the viscosity, P is the pressure, and $\underset{\sim}{F}$ is the external force. Also of use is the continuity equation:

$$\frac{\partial \rho}{\partial t} + \text{div } \rho \underset{\sim}{V} = 0. \tag{25}$$

Most often the continuity equation is found in the form $\text{div } \underset{\sim}{V} = 0$, where the medium has been assumed to be incompressible. For a drop moving with respect to an incompressible medium, the diffusion equation becomes:

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \underset{\sim}{V} \text{ grad } c \ . \tag{26}$$

Fuchs (1934) looked at possibly the simplest case, i.e. for laminar flow, for which Stokes' law holds, and for which a stationary state exists. His method, for infinitely small flow velocity, was to let $c=c_s \cdot \frac{a}{r} + V\Phi$, where V is the flow velocity at a large distance from the drop, and the term $V\Phi$, the perturbing effect of the flow on the concentration distribution. With this model, Fuchs found that any increase in evaporation on the front face of the drop was exactly balanced by a decrease of the rate on the rear face. Fuchs concluded that, for small Re, i.e. Stokes flow, the motion would have a vanishingly small influence on the evaporation rate.

Frössling (1938) studied the moving, evaporating drop both theoretically and experimentally, determining the

ventilation factor, f, where the evaporation rate in an air stream is given by $I=I_M \cdot f$. He assumed (a) the drops to be spherical, (b) the evaporation to be a stationary state process, and (c) the vapor concentration at the surface to be at saturation. Using the time independent forms of Eqs. 24 through 26, Frössling's theorectical conclusion was that f was a function of Re and Sc. From studies of the evaporation of ventilated napthalene spheres, he arrived at the conclusion that the rate of evaporation was proportional to $Re^{\frac{1}{2}}$, and from an analogous theory for heat flow, to $\sqrt[3]{Sc}$.

Frössling also studied the evaporation rates for ventilated water, nitrobenzene, and aniline drops suspended from fine glass rods; and thermocouples. The drop radii varied from 0.1 to 0.9 mm. Using an average of the data for all four substances studied, Frössling arrived at a ventilation factor:

$$f = (1 + 0.276 Re^{\frac{1}{2}} \sqrt[3]{Sc}) \ , \qquad (27)$$

for the range $2 \leq Re \leq 1000$.

Ranz and Marshall (1952), in a study restricted to $0 \leq Re \leq 200$, found the ventilation factor to be:

$$f = (1 + 0.3 Re^{\frac{1}{2}} \sqrt[3]{Sc}) \ . \qquad (28)$$

Their technique involved water, benzene and aniline drops of approximately 1 mm in diameter suspended from a microburet.

The evaporation rates were determined by measuring the flow rate of the fluid through the buret necessary to maintain a constant drop size.

Hsu, Sato and Sage (1954), in a manner similar to Ranz and Marshal, determined the evaporation rates of drops of n-heptane of radius approximately 0.9 mm for the range $70 \leq Re \leq 300$. This work went further than the previous work in that an emphasis was put on the effect of drop shape on the evaporation rate. By trial and error they arrived at the rate law:

$$Sh = 2(1 + 0.178Re^{\frac{1}{2}}\sqrt[3]{Sc}) \cdot (1 + 2.292\{1-\lambda\}) \cdot (1 - 0.257\{1-h/d\}), \quad (29)$$

that gave am minimum standard error of estimate in the Sherwood number. Eq. 29 assumes that the Sherwood number is a linear function of the sphericity, λ, and the height-diameter ratio, h/d. They also compared their results to Frössling's, and Ranz and Marshall's results. Hsu, Sato and Sage's data, reduced to that of an equivalent sphere, gave a rate of

$$I = I_M(1 + 0.272Re^{\frac{1}{2}}\sqrt[3]{Sc}) , \quad (30)$$

which was quite close to Frössling's result, but lower than that for Ranz and Marshall's.

It is noted that the evaporation rate laws arrived at

by the above authors are of the form:

$$I = I_M(1 + \beta Re^{\frac{1}{2}}\sqrt[3]{Sc}) \quad , \tag{31}$$

where the ventilation factor is a linear function of $Re^{\frac{1}{2}}$.

For further studies on large drops and large Re, the reader is referred to Fuchs (1959).

Kracke and Puckett (1964) studied the evaporation of ventilated hexadecane droplets of radius less than 75 micron and supported by sub-micron size filaments. The drops studied fell into two groups. The first group evaporated so that $d(a^2)/dt$ was constant, even though the ventilation rate was as high as 85 cm/sec. The second group evaporated at two different, but constant, rates with a sharp change between the two rates. Their explanation for their observations was that the evaporation was from a vapor concentration boundary layer surrounding the drop, and at higher air velocities the thickness of the layer decreased, so that although the rate of evaporation had increased, the change in surface with time was still a linear function.

A notable exception to the rate law given by Eq. 31 was proposed in a theorectical and experimental study by Kinzer and Gunn (1951). Theoretically, the problem was that of the quasi-transient heat transfer to successive packets of air making thermal contact with a ventilated sphere. The derived rate of evaporation was given as:

$$I = 4\pi aD(\rho_a - \rho_\infty)\left[1 + \frac{F\ Re^{\frac{1}{2}}}{\sqrt[3]{4\pi\rho_A D/\eta}}\right] , \qquad (32)$$

where the term in the square brackets is the ventilation factor, f, and ρ_A and η are the density and viscosity of the ambient air. At STP, the ventilation factor is approximately equal to:

$$f = 1 + 0.22FRe^{\frac{1}{2}} . \qquad (33)$$

To determine the factor F, the authors state that an exact knowledge of the air flow around the sphere must be known (see Abraham, 1968). Experimentally, they found that F was dependent on $Re^{\frac{1}{2}}$, which contradicts those who arrived at rates of evaporation of the form given by Eq. 31. The departure was most noticable at small Re. For Re>100, F≈1, reaching a minimum of 0.85 at Re≈800, and then slowly increasing to 1.3 at Re≈2500. For decreasing Re, however, F rose to approximately 2.2 at Re≈5 and then dropped to zero for Re<1. Kinzer and Gunn believe that the behavior of small droplets, a<50 micron, is largely dominated by shear forces due to the viscosity of the surrounding air, and that the droplets evaporate into entrained air at rates comparable with those given for nonventilated drops.

Also experimentally, Kinzer and Gunn found that, within ±0.3C, the equilibrium temperature of an evaporating, ventilated drop is identical to the ventilated wet bulb

temperature. The radii of the drops studied ranged from 8 micron to 0.2 cm, and all were "free", in the sense that they were not supported by filaments or thermocouples.

Of particular interest is the comparison between the rates of evaporation given by Kinzer and Gunn, and Eq. 31. For a freely falling water drop of radius 5 micron and Re≈0.006, Eq. 32, because of the behavior of F, reduces to:

$$I = 4\pi a D(\rho_a - \rho_\infty) \ , \tag{34}$$

where ρ_a is the saturated vapor density at the drop surface corresponding to the temperature of the drop. While in this instance the ventilation factor is zero, Kinzer and Gunn did not indicate that the temperature of the drop was other than the ventilated wet bulb temperature, as used for their data at higher Re.

For the same drop as above, Eq. 31, to a good approximation, reduces to the rate of evaporation given by Maxwell. The error in the rate due to ignoring the ventilation factor is of the order 2%. Fuchs (1959) states that the temperature correction for a freely falling drop is approximately the same as for a stationary drop, regardless of its velocity with respect to the medium, which would indicate that the drop temperature is different than the wet bulb temperature.

An equation for the growth of a ventilated droplet that is equally applicable to evaporation was derived by Squires (1952). His theory was based on a formula for the

equilibrium vapor pressure over a drop:

$$p_d = p(T_d)\left[1 + \frac{2\sigma\epsilon}{R\rho_\ell aT} - \frac{3Mm_w}{4\pi\rho_\ell a^3}\right], \tag{35}$$

where $p(T_d)$ is the equilibrium vapor pressure over a flat water surface at the temperature T_d of the drop surface, σ is the surface tension of pure bulk water, m_w is the molecular weight of water, M is the measure of the size of the condensation nucleus, and ϵ is the specific gravity of water vapor with respect to air, using molecular weights rather than densities. The term $\frac{2\sigma\epsilon}{R\rho_\ell aT}$ shows the increase in the vapor pressure due to the surface curvature, and the term $\frac{3Mm_w}{4\pi\rho_\ell a^3}$ shows a decrease due to the presence of the nucleus. It was assumed that the solution formed by the nucleus was very dilute and M was then defined as the molar mass of the nucleus.

Then using:

$$Nu = 2(1 + 0.276Re^{\frac{1}{2}}\sqrt[3]{Pr}) = 2(1 + 0.246Re^{\frac{1}{2}}) \tag{36}$$

for the heat transfer, and:

$$Sh = 2(1 + 0.276Re^{\frac{1}{2}}\sqrt[3]{Sc}) = 2(1 + 0.232Re^{\frac{1}{2}}) \tag{37}$$

for the mass diffusion, and solving the heat balance problem for the drop, Squires arrived at the growth law:

$$\frac{dm}{dt} = 4\pi aE(1 + 0.232Re^{\frac{1}{2}})(S - \beta/a + \gamma M/a^3) \quad , \qquad (38)$$

where m is the mass of the drop, and

$$E = \frac{\varepsilon^2 LDJp}{R^2T^3}\left(1 + \frac{\varepsilon^2 L^2 DJp}{\kappa R^2 T^3}\cdot\frac{(1 + 0.232Re^{\frac{1}{2}})}{(1 + 0.246Re^{\frac{1}{2}})}\right)^{-1} \quad .$$

J is the mechanical equivalent of heat, p is the average vapor pressure, $S=T_{dp}-T_\infty$, T_{dp} is the dew point temperature, $\beta=2\sigma T/JL\rho_\ell$, and $\gamma=3m_w RT^2/4\pi JL\varepsilon\rho_\ell$. In the derivation, the Clausius-Clapeyron relation was used to give an expression for $p(T_{dp})-p(T_d)$, and Squires states, that while the values of p, T, and L should be taken at some temperature between T_{dp} and T_d, they may be taken to a good approximation as being constant, as long as not too large a temperature range is considered in the Clausius-Clapeyron equation.

It is evident from the literature that the theory has outdistanced the experimental work on drop evaporation. This is notably so for drops with radii from 5 to 20 microns. The evaporation of larger supported drops, both ventilated and nonventilated, has been extensively studied. This is also true for smaller charged droplets that can be observed in a Millikan type apparatus. Of the literature reviewed, only Kinzer and Gunn (1951) have reported any data for the size range noted above, and that was only for one drop. Moreover, their semi-empirical formulation implies that even small,

freely falling, water droplets are ventilated to the extent that they take on the temperature of a ventilated wet bulb. On the other hand, most other workers believe that the effects of ventilation on small water droplets should be vanishingly small. No experimental verificaion of either theory has been found in the literature. Thus the present work, besides laying a foundation for future investigations, is an attempt to experimentally determine the behavior of small ventilated water droplets.

APPARATUS

As mentioned previously, the work that has been reported for the evaporation of ventilated water drops has been mostly for drops that are supported by fine filaments, or thermocouples. Besides being limited by the size of the support and complications due to heat flow along the support, the method is not physiographical since in nature drops are free.

The work presented here is part of a larger problem that may be of interest to the Atmospheric Sciences, the effect of surface active materials on droplet evaporation. Therefore, it was desirable to design the apparatus so that the experimental conditions would correspond as closely as possible to actual atmospheric conditions. With this in mind, a diffusion cloud chamber was used so that the drops could be formed on condensation nuclei, besides which it provided an ample supply of drops of the size range of interest. Rather than supporting the drops, they were allowed to fall freely through air at various humidities in a drift tube. It was possible to determine photographically the terminal velocities and thus the evaporation rates under conditions less artificial than in the methods mentioned above.

DROP GENERATOR

The diffusion cloud chamber, shown in Fig. 1, had a

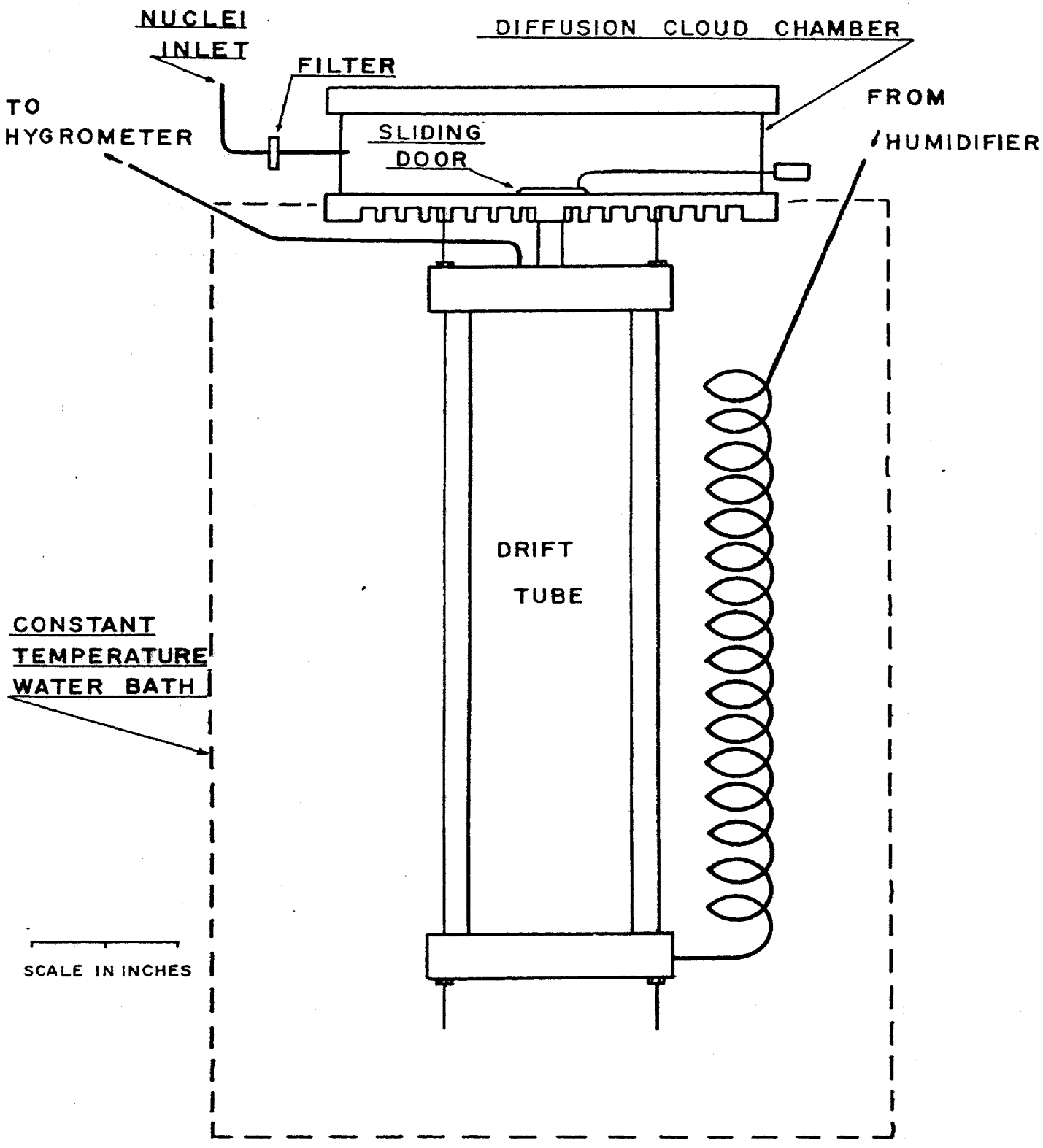

Fig. 1. Drop generator and drift tube.

diameter of approximately 15 cm, with a 2.5 cm separation between upper and lower plates. The upper plate was heated by nichrome wires embedded in epoxy filled concentric grooves. A porous (5 micron diameter pore size), sintered stainless steel plate covered a water reservoir on the underside of the of the upper plate. The bottom plate had a threaded hole in its center, through which the drops passed into the drift tube. Provision was made to close this hole with a sliding door. The walls were a section of 5 inch I.D., 0.25 inch thick wall, lucite tube.

Condensation nuclei were obtained by injecting room air into the cloud chamber through an 8.0 micron Millipore SCWP02500 filter. The purpose of the filter was to keep contamination of the droplets by these nuclei to a minimum: the smaller the nuclei, the less contamination per drop. Filters of smaller pore size were tried, and nucleation either did not occur, or did not produce a sufficient number of droplets.

DRIFT TUBE

The drift tube (Fig. 1) was constructed from four pieces of polished, double-thick plate glass, sealed with Dow Corning Silastic 732 RTV. The over all dimensions of the tube were ten inches by two inches by two inches. The drift tube was separated from the bottom plate of the cloud chamber by a one inch length of 0.25 I.D. copper tubing. Although at one time the drift tube was attached directly to the bottom

plate, in that configuration the drops would not pass into the tube. This may have been due to convection currents caused by heat flow from the bottom plate of the cloud chamber. The small diameter of the copper tubing also had the effect of collimating the falling drops, so that they fell only in the center of the drift tube, reducing wall effects to a minimum.

WATER BATHS

Two water baths, thermostatically controlled to better than ±0.01C by mercury thermoregulators, were used. The whole of the drift tube, and the bottom plate of the cloud chamber were placed in bath A (Fig. 1). This bath served three purposes. First, it acted as a heat sink for the bottom plate of the cloud chamber. Secondly, a thermostated, constant temperature water bath proved to be the best way to eliminate temperature gradients and the accompanying convection currents in the drift tube. An enclosure with thermostated circulating air was tried at first, but to no avail. Thirdly, the temperature of the bath, which determined the temperature of the air inside the drift tube, was used as the reference temperature for the experiment. This temperature was measured to the nearest 0.05C by a mercury-glass thermometer. The second thermostated water bath, bath B (Fig. 2), was used to regulate the temperature of the humidifying apparatus.

HUMIDIFYING APPARATUS

Initially, the air through which the drops were to fall was humidified by bubbling it through water whose temperature was maintained at the required dew point temperature. It was pointed out that bursting bubles form very small droplets that could produce a humidity different than that calculated from the temperature of the humidifier. To eliminate this source of error it became necessary to humidify the air by passing it over a water surface rather than through water. This was accomplished by fabricating a box (Fig. 2), twelve inches on a side, and two inches deep. In order that the air have the longest possible contact with the water for any given flow rate, the inside of the box contained baffles, separated by about 1 cm, and extending from one wall to approximately 1 cm from the opposite wall. The baffles were connected to the top of the box, and the space between the bottom of the baffles and the bottom of the box, about 1 cm, was to maintain a uniform temperature throughout the humidifier. The box was filled to within 1 cm of the top with distilled water, producing an air path of 1 cm^2 cross sectional area, and approximately 25 feet long. The humidifying box was totally immersed in bath B, and the temperature difference between the water in the humidifier and the bath was monitored by means of a copper-constantan thermocouple to detect any deviation from equilibrium.

To insure that the air leaving the humidifier had a dew point equal to the temperature of bath B, the air was passed

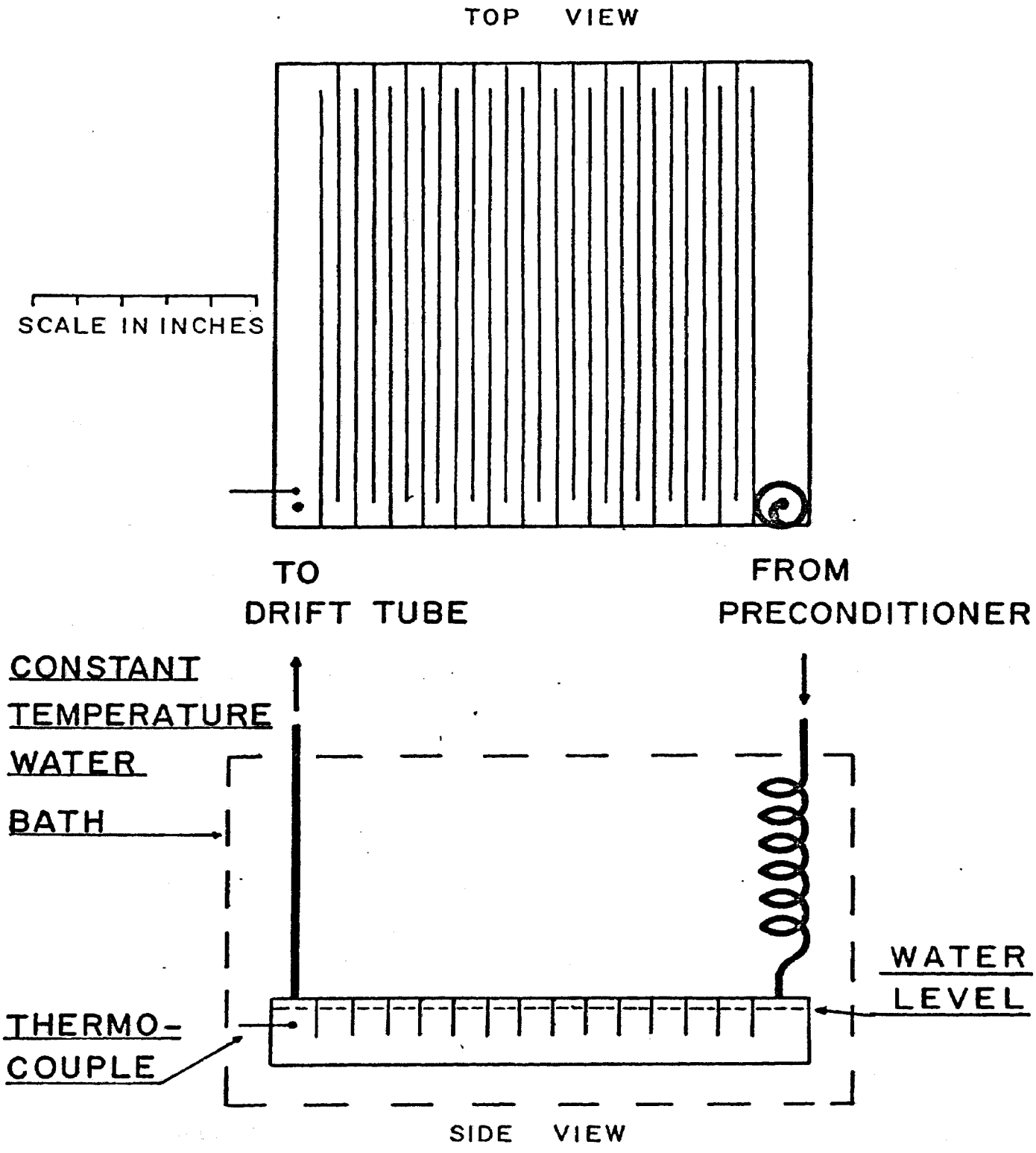

Fig. 2. Humidifier

through a preconditioner before it went into the humidifier. The preconditioner was a flask of water heated to at least 5C higher than the temperature of the bath surrounding the drift tube. After leaving the preconditioner, the air was passed through a copper coil in bath B (Fig. 2) to reduce its temperature. Use of the preconditioner lessened the amount of water vapor that had to evaporate into the air stream from the water in the humidifier.

The humidifier was connected to the drift tube by means of 0.19 I.D. copper tubing. The sections of this tubing exposed to room temperature were wrapped with heater wires, and maintained at a temperature higher than that of bath A to eliminate the possibility of condensation. Before going into the drift tube, the air was passed through a copper coil immersed in bath A (Fig. 1), so that the temperature of the air was that of the drift tube.

HUMIDITY MEASUREMENT

Initially, the humidity of the air passed through the drift tube was measured by a dew point hygrometer. The instrument used was a Technology/Versatronics, Inc., model 707 Thermoelectric Dew Point Hygrometer, which uses an optical sensing technique. The specifications given by the company call for an accuracy of ±0.5F or ±0.28C. This did not meet the requirements of the experiment, as an accuracy of better than 0.01C was needed. Therefore, two pairs of copper-constantan thermocouples were employed. One pair was

used to detect any difference in temperature between bath B and the water inside the humidifier. The second pair measured the difference in temperature, ΔT, between bath A and bath B, or assuming saturation of the air leaving the humidifier, the dew point depression. Prior to their initial use, both pairs were placed in close proximity in bath B and checked for a null reading. The potential difference between the two thermocouples in each pair was measured with a Leeds and Northrup K-5 potentiometer, which had a sensitivity of 0.02 microvolts.

It was assumed in using this method that there was no condensation or absorption of water vapor in the lines between the humidifier and drift tube, and that the dew point of the air was the temperature of the water in the humidifier. As an added check, the hygrometer was left connected to the system, and the dew point measured by the hygrometer was compared to that obtained from the thermocouples throughout the time data was collected. Within the limit of error of the hygrometer, the dew point temperatures were the same. The complete system, from the preconditioner to the hygrometer is shown schematically in Fig. 3.

MOVIE CAMERA

As the drops fell through the humidified air in the drift tube, a series of pictures were taken. The camera used was an Automax, 35 mm, model G-1 movie camera, produced by Traid Corporation. The model G-1 can be run either at a cine

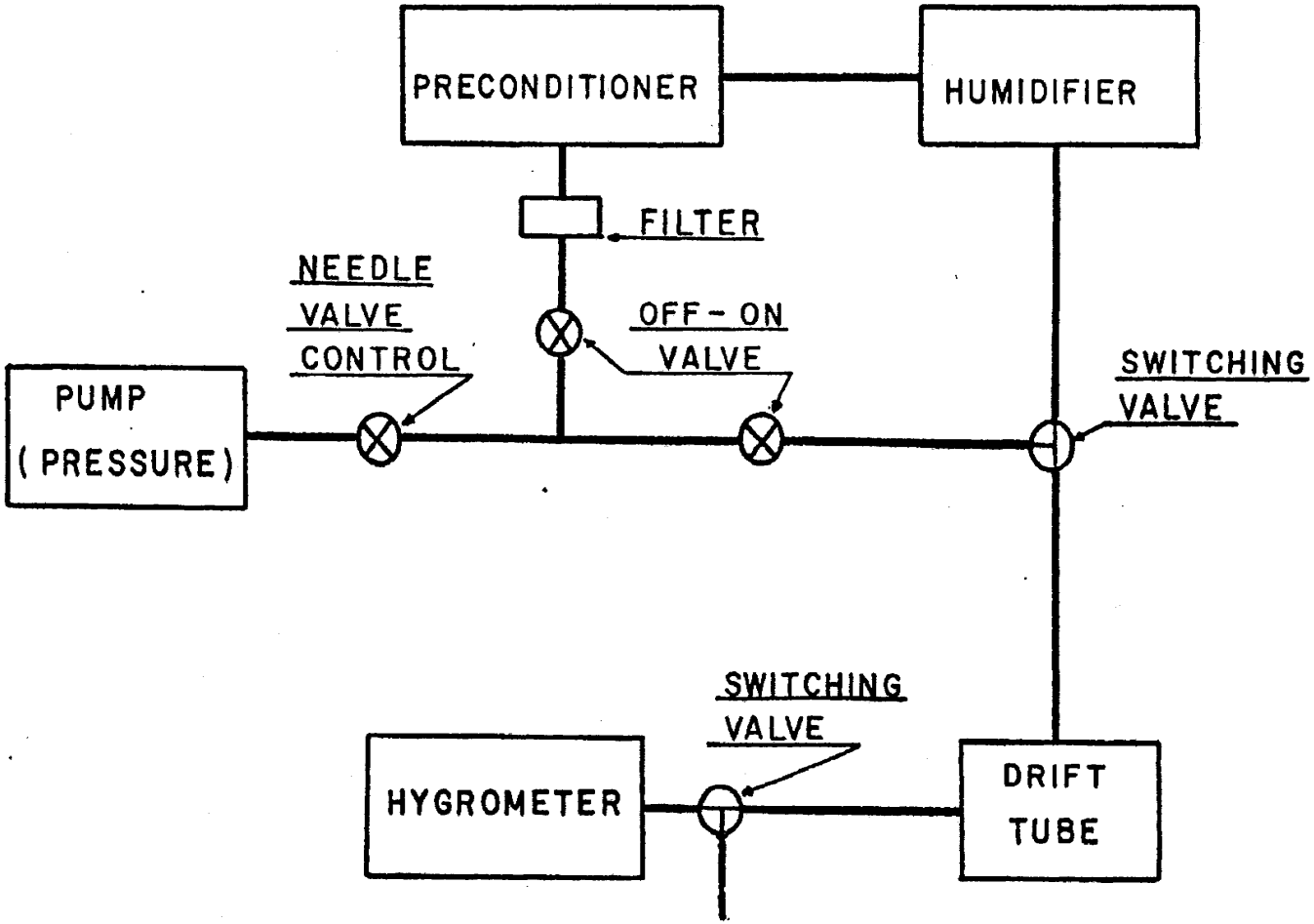

Fig. 3. Block diagram of apparatus.

frame rate of 16 frames per sec. or in a single frame mode in which an external controller can vary the rate up to a maximum of 10 frames per sec. A rate of two frames per sec. was used throughout the experiment. The exposure duration of the model G-1 is 1/64 sec. A f=55 mm, f/3.5 Micro-Nikkor lens was adapted to the camera, and a maximum opening was used.

The camera was mounted with the film plane about ten inches from the center of the drift tube and with the optical axis making an angle of approximately 30^{o} with the beam of light used for illumination. The actual angle, determined experimentally, was the angle at which the scattered light from the drops was the greatest without having interference from the illuminating beam. Also, at this angle, the camera was shooting against a relatively dark background.

FILM AND DEVELOPMENT

The film used was Eastman Kodak Linograph Shellburst film, which has an ASA rating of 400. It was developed in a one to one dilution of Acufine film developer, made by Baumann Photo-Chemical Corp., for a period of 18 min. This raised tha ASA rating to approximately 800, which gave a high contrast but with a fine grain size.

LIGHT SOURCE

The light source used was a 12 inch long GE 1000-T-3/CL quartz bulb. The light from the bulb was collimated by a

cylindrical lens, and the width of the beam was further reduced by masking the front of the lamp housing, so that the emitted beam was 1 cm wide. The lamp was positioned so that it illuminated the cloud chamber and the upper two thirds of the drift tube. The center of the beam coincided with the center of the drift tube and the hole in the bottom plate of the cloud chamber.

FILM SCALE CALIBRATION

In order to know how far a drop had fallen in the time between film frames, it was necessary to know what distance on the film corresponded to a given vertical distance in the drift tube. This was accomplished by photographing a grid hung in the center of the drift tube. The grid was a small aluminum frame, 4 inches long, by 1.5 inches wide, with 40 micron diameter wires at 2 mm intervals. The actual spacings of the wires were measured to 0.001 mm by means of an optical comparator. The developed film was projected at the same distance from the screen as when viewing the pictures of the falling drops. Since the spacings between the grid wires were known, it was possible to construct a magnified scale with divisions corresponding to 0.2 mm in the drift tube. The over all magnification was greater than 10x's.

EXPERIMENTAL PROCEDURE

Initially the temperature of the bath surrounding the drift tube, bath A, was extablished. Once the setting was made, it needed no further adjustment, although the temperature was checked at intervals. After it was apparent that the temperature of bath A had stabilized, the temperature of the bath surrounding the humidifier, bath B, was adjusted to the desired dew point. As there was a time lag between the time it took the bath to stabilize and for the humidifier to reach thermal equilibrium, it was necessary to monitor the voltage output of the thermocouple pair between the two. The difference in temperature between the two baths, ΔT, was also monitored for a period of at least an hour before a run was initiated.

When the temperature differences between the baths and between bath B and the humidifier had stabilized, air was pumped through the system (Fig. 3), at a rate of one liter per min. for at least a half hour. During this time, it was found convenient to use the hygrometer as a secondary check on the humidity. The relatively long period of time between the start of the humidifying process and the initiation of data taking was to insure that even if water vapor was absorbed by the system, equilibrium had been reached and the dew point of the air going through the drift tube was the same as the temperature of bath B.

At this point nuclei were injected into the cloud chamber, the air pump turned off, and the drift tube closed off from the humidifier by means of a valve. Special attention is made of the fact that the air pump was not turned off until AFTER the nuclei were injected. It was found that if the pump were turned off first, there was the chance of forcing water, that had condensed on the bottom plate of the cloud chamber, under the door and into the drift tube. If water could be forced into the drift tube, it was highly probable that air from the cloud chamber could also be forced into the drift tube causing a change in the humidity.

The droplet population in the cloud chamber was observed until it was at a desirable level. The knowledge of what this constituted was arrived at by trial and error, and depended on what rate one wanted drops to fall into the drift tube. This concern about the droplet population in the cloud chamber is because with an overabundance, a cloud, rather than a few drops, fell into the drift tube. This caused three problems. First was the inability to keep track of individual drops from one film frame to the next. Second was the possibility of interaction between drops. Finally, a cloud of drops could have had an appreciable effect on the humidity in the drift tube. The optimum condition was a single drop. However, for about half the runs, up to six drops were present in the field of view at any one time. If the population in the cloud chamber did not decrease to a

usable value within one minute, the humidifier was again connected, and the drift tube rehumidified for about a minute. This was also done if there was a paucity of drops in the chamber. In either case, after rehumidification nuclei were again injected and the process repeated until the population was at the desired level. At this point, the door was opened and the drops allowed to fall into the drift tube. When the drops fell into the field of view, the camera was started, as was a strip chart recorder that was used as an event marker and a check on the framing rate of the camera. At the end of twenty to thirty seconds, or when drops ceased to fall into the drift tube, the camera was stopped. The maximum data acquisition time of thirty seconds was due to the length of film that could conveniently be handled during the developing procedure, and the concern that a longer time would allow the humidity in the drift tube to change.

Following the end of the run, the drift tube was reconnected to the humidifier, the air pump started, and the door separating the drift tube from the cloud chamber closed. At this time the differences in temperature between the baths and between bath B and the humidifier were noted, as well as the hygrometer reading. The humidification process was continued for about a minute to insure that the drift tube had been thoroughly flushed. The data acquisition process was then repeated until four runs had been obtained for each dew point temperature.

RESULTS

An example of the data for the evaporation of a single droplet is shown in Table I and Fig. 4. Δs is the distance the droplet fell in 0.5 sec. and was determined from the position of the droplet in succesive film frames. The velocity, determined by dividing Δs by 0.5, was the average velocity of the droplet between two exposures. It was, however, assumed to be the true velocity of the droplet at a time midway between the two exposures. A curve was fitted to the data for each droplet by a least squares computer program. In all cases, the best fit was a straight line whose slope multiplied by 2 was dv/dt.

The relationship between the terminal velocity of a falling, spherical particle and the square of its radius is given by Stokes' law,

$$v = a^2/K_s \ , \tag{39}$$

where $K_s = \frac{9\eta}{2(\rho_\ell - \rho_A)g}$ is a constant that is a function of the physical properties of the medium and particle. The values used for η, the viscosity of air; ρ_ℓ, the density of water; and ρ_A, the density of air are listed in Appendix II, as well as the values of K_s in units of micron^2-sec/mm. Since it was the rate of evaporation that was of interest, the slopes of the fitted curves, $d\Delta s/dt$, were multiplied by $2K_s$ giving the rate of evaporation, $d(a^2)/dt$, for each drop.

TABLE I

DATA OBTAINED FOR AN EVAPORATING DROPLET

Film frame number	Position of drop image on scale	Δs (mm)	Elasped time (sec)
1	4.7		
		3.4	0.25
2	8.1		
		3.4	0.75
3	11.5		
		3.0	1.25
4	14.5		
		2.9	1.75
5	17.4		
		2.5	2.25
6	19.9		
		2.5	2.75
7	22.4		
		2.2	3.25
8	24.6		
		2.0	3.75
9	26.6		
		1.9	4.25
10	28.5		
		1.6	4.75
11	30.1		
		1.4	5.25
12	31.5		
		1.3	5.75
13	32.8		
		1.0	6.25
14	33.8		
		0.8	6.75
15	34.6		

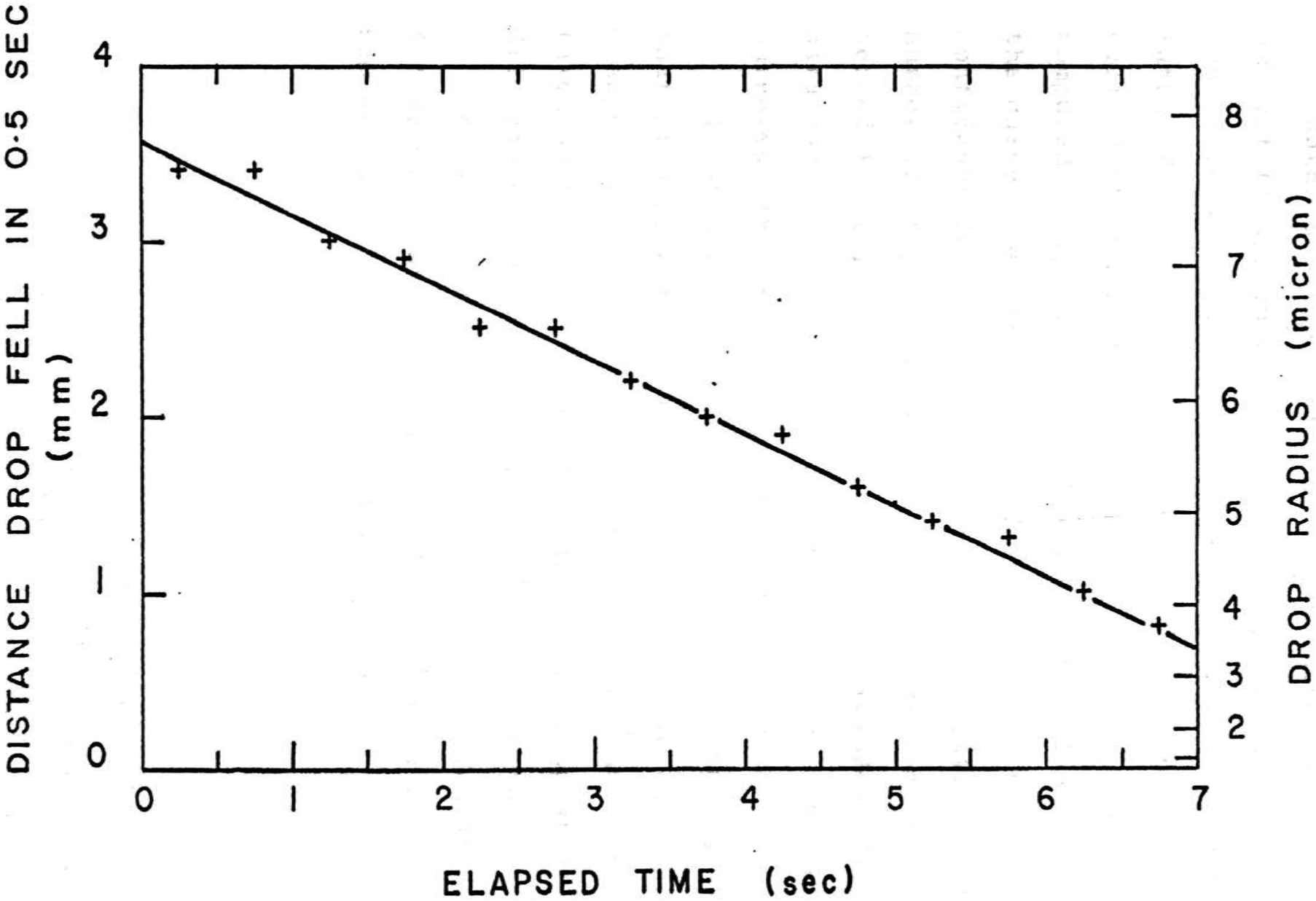

Fig. 4. Evaporation of a single droplet.

Rates of evaporation were determined at three different ambient temperatures, T_A, and at various dew point depressions. Figs. 5-7 show the experimentally determined rates of evaporation for all of the droplets observed, as well as the curve that was the best fit to the data as computed by the method of least squares. The coefficients of the curves, and the upper and lower bounds at the 95% confidence level are listed in Table II. Also noted is the number of drops observed at each ambient temperature. The second listing for T_A=35C, 67 drops, excludes some of the data and is discussed in the next section. For comparison purposes, the three calculated curves are shown in Fig. 8.

It should be noted that the data at 25C, as well as that at 35C, were obtained during a single day without any changes in the apparatus during the run. Those at 30C were taken on three different days and show no apparent differences in the results from one day to the next.

Finally, rates of evaporation were calculated at three different relative humidities for the three ambient temperatures and are plotted in Fig. 9.

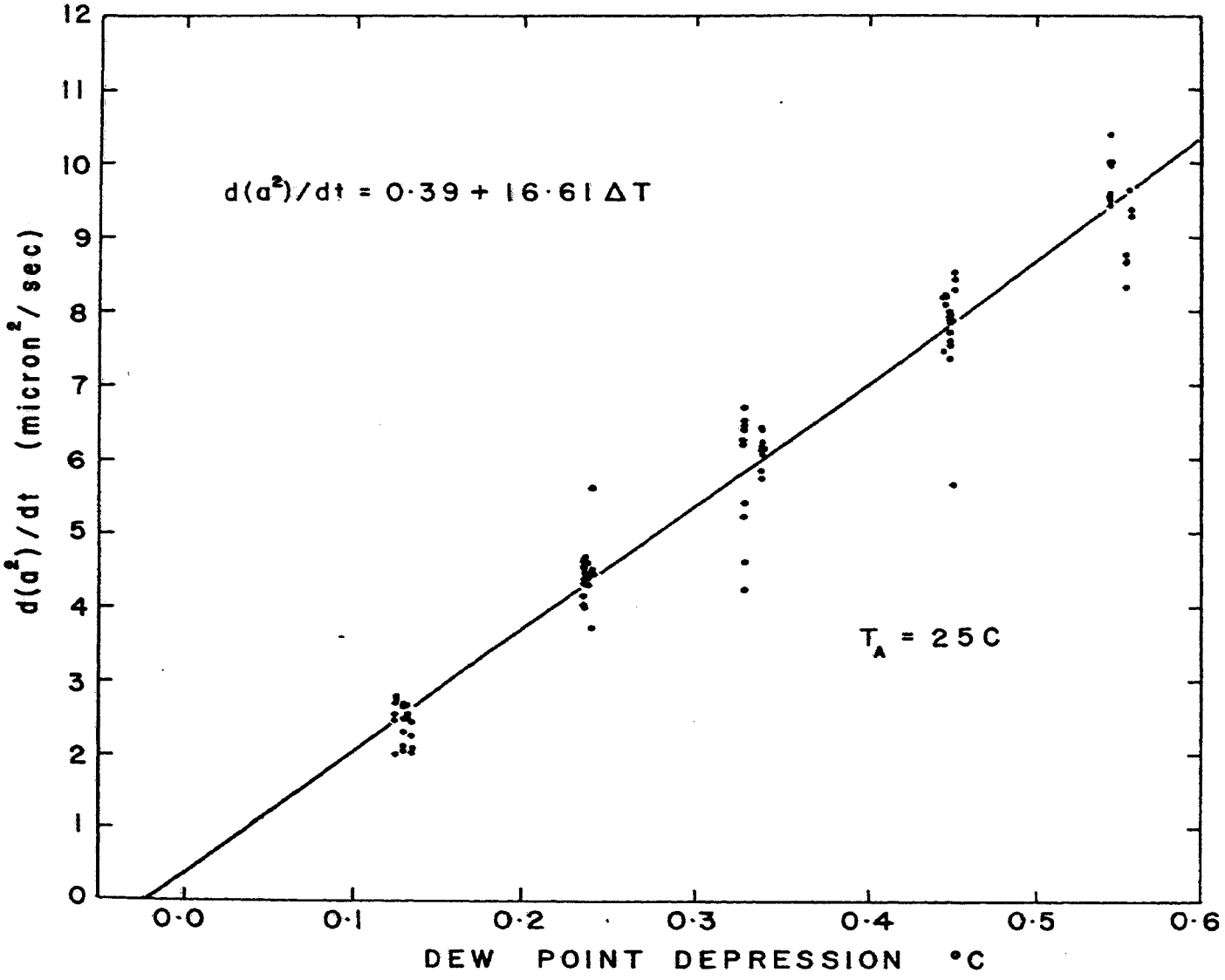

Fig. 5. Experimental evaporation rates at 25C.

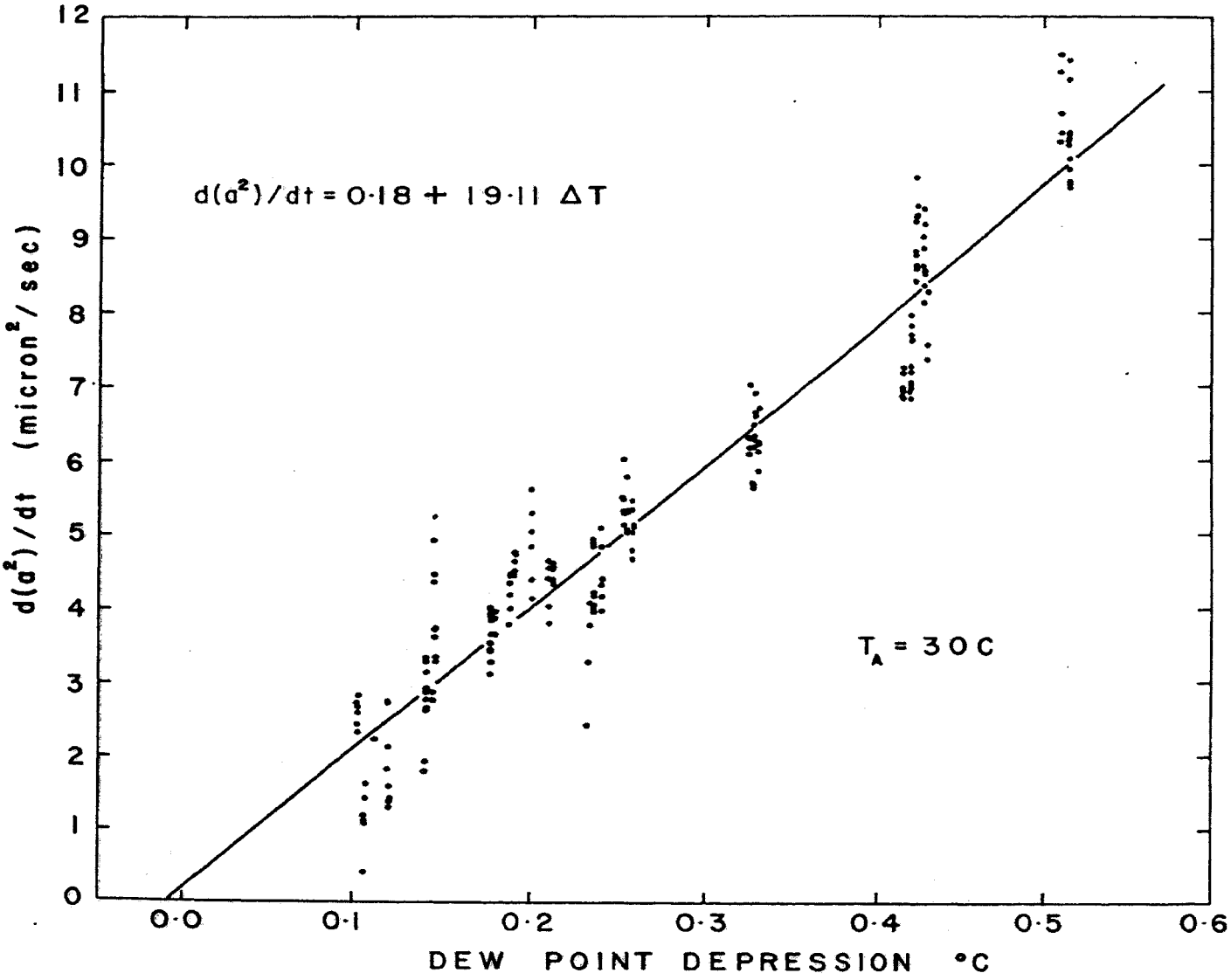

Fig. 6. Experimental evaporation rates at 30C.

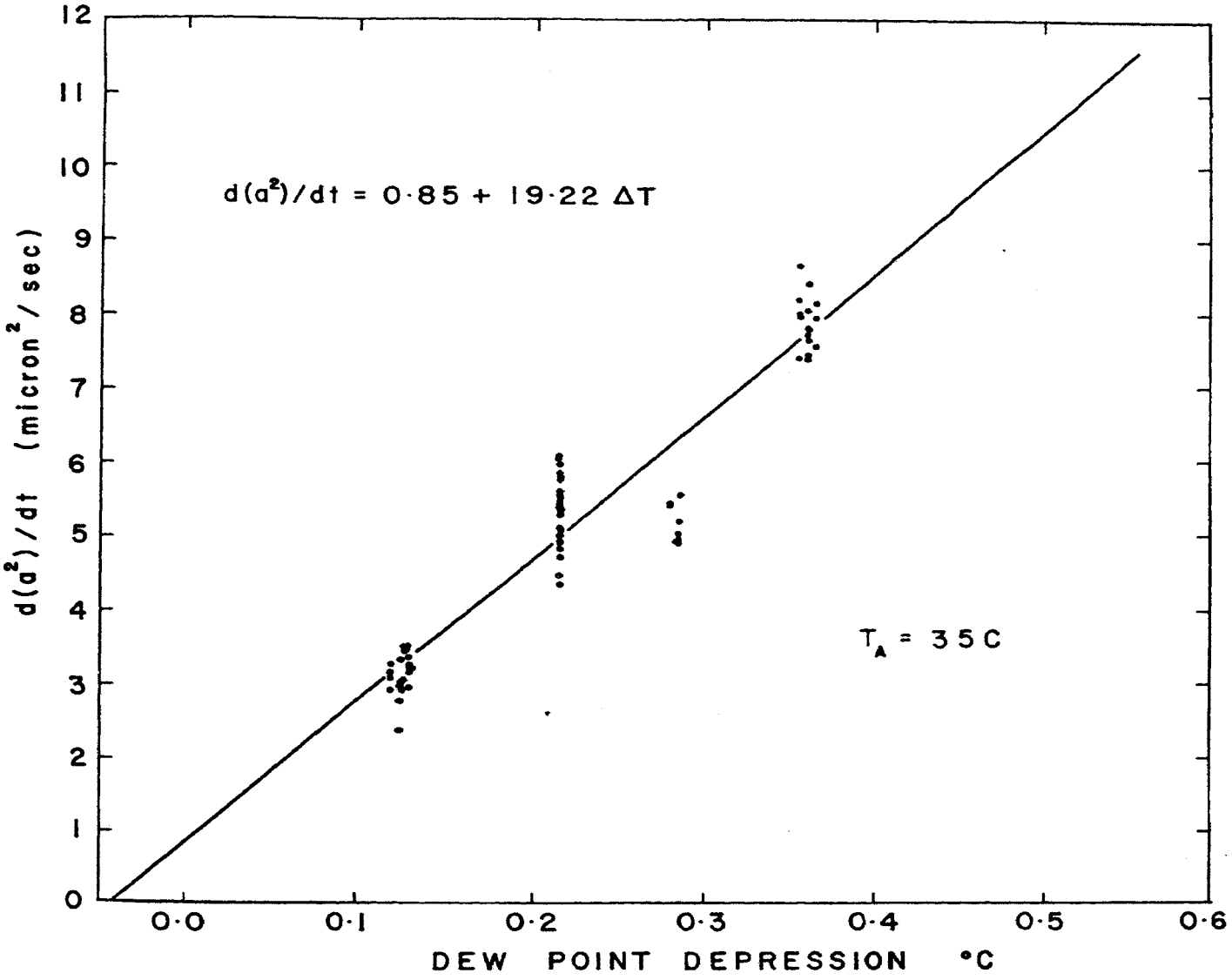

Fig. 7. Experimental evaporation rates at 35C.

TABLE II

RESULTS OF LEAST SQUARES FIT OF STRAIGHT LINE TO $\underline{d(a^2)/dt \text{ versus Dew Point Depression}}$ DATA

$$d(a^2)/dt = B\Delta T + R_o$$

TEMPERATURE	NO. OF DROPS	COEFFICIENT	NUMERICAL VALUE OF COEFFICIENT	95% CONFIDENCE INTERVAL	UPPER BOUND	LOWER BOUND	STANDARD ESTIMATE OF ERROR	X INTERCEPT
25C	96	slope-B	16.61	0.72	17.33	15.88	0.518	0.024
		y intercept R_o	0.39	0.26	0.66	0.13		
30C	206	slope B	19.11	0.77	19.88	18.34	0.700	0.010
		y intercept R_o	0.18	0.23	0.42	-0.05		
35C	75	slope-B	19.22	1.54	20.75	17.68	0.579	0.044
		y intercept R_o	0.85	0.37	1.23	0.48		
35C	67	slope-B	20.29	1.15	21.45	19.14	0.422	0.037
		y intercept R_o	0.75	0.27	1.03	0.48		

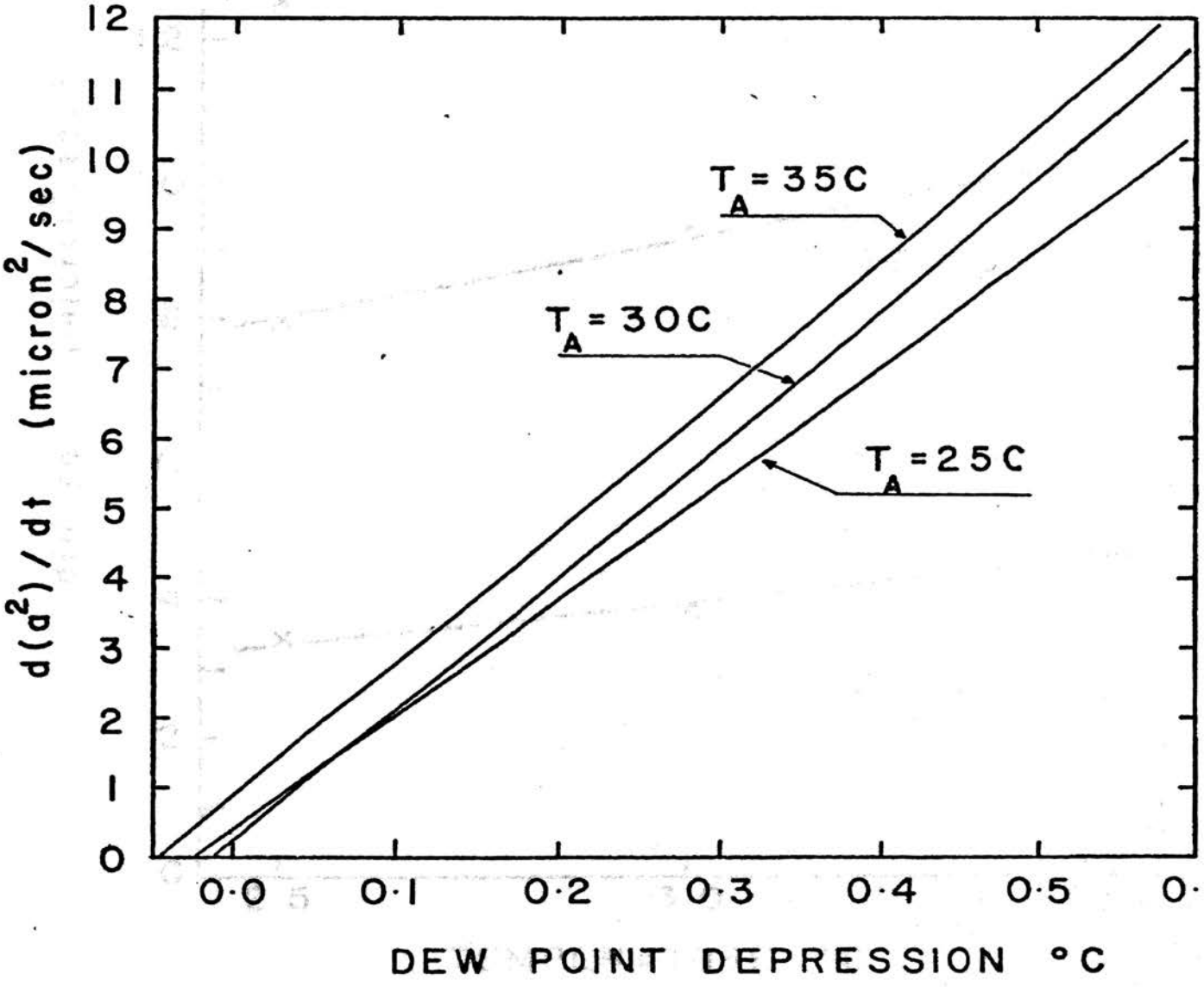

Fig. 8. A comparison of the experimental evaporation rates.

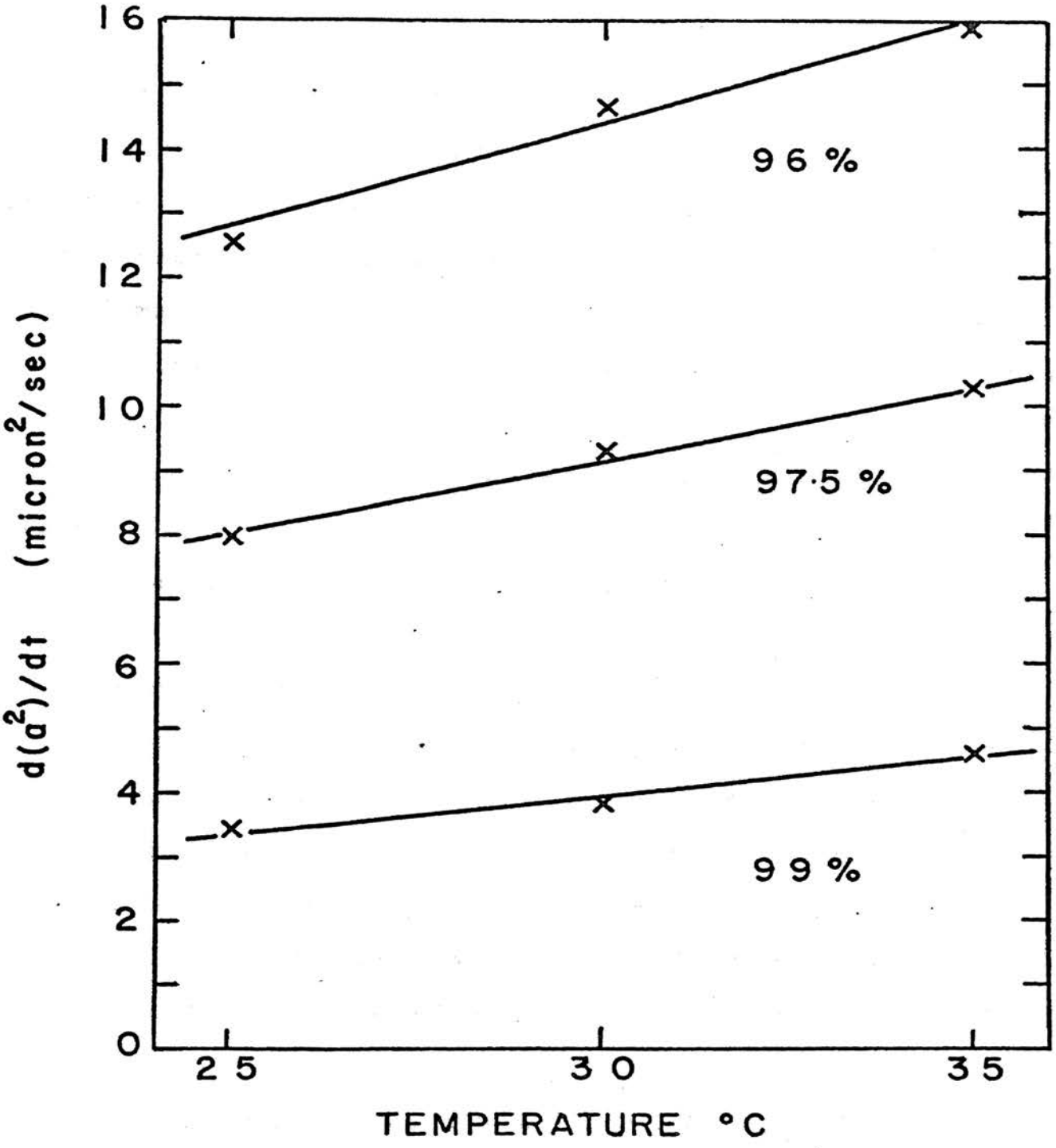

Fig. 9. Evaporation rates at constant relative humidities.

EXPERIMENTAL ERROR

The primary measurements in the experiment were the position of the image of the drop on the film, the time between successive film frames, and the difference in temperature between the two water baths.

The error in measuring the position of the drop image was ±0.05 mm. which resulted in a most probable error in Δs equal to ±0.07 mm. For the smaller values of Δs encountered, this was a 7-10% error.

The time interval between film frames was determined by measuring the time for 30 frames to an accuracy better than 0.1 sec. Therefore, the average error per frame was ±0.0033 sec.

The temperature difference between the two water baths was measured with a pair of thermocouples. Because of the method of temperature control, the temperature of each bath fluctuated slightly, ±0.005C, over a period of a few minutes. Since there was also a lag between the the change of temperature in the humidifier and the surrounding water bath, it was possible that the error in the dewpoint depression was as much as ±0.01C.

Looking at Figs. 5-7, there is a noticeable amount of scatter in the evaporation rates. For a given dew point depression, the difference between the maximum and minimum values for $d(a^2)/dt$ is of the order 1.5 micron^2/sec. The most probable error in $d(a^2)/dt$, ±0.27 micron^2/sec, due to

the error in Δs and the time, is not sufficient to explain the scatter in the data. This would lead one to believe that the scatter was probably due to errors other than those inherent in the measurements.

A possible source of error occured in the analysis of the data with the use of Stokes' law. Davies (1945) gives an equation that was derived from the data of a number of experimenters. For small Re, such as encountered in this investigation, the equation reduces to Stokes' law. However, for drops having radii of the same order of magnitude as the mean free path, Stokes' law must be corrected for "slip". Davies gives the "slip factor" as

$$s.f. = 1 + \left(\frac{10^{-4}}{P\,a}\right)\{6.32 + 2.01\cdot\exp(-2190Pa)\} , \quad (40)$$

where P is the pressure in cm Hg, and a the radius of the drop in cm. The true terminal velocity is given by multiplying the Stokes' velocity by the "slip factor". For a 5 micron drop at P=73 cm Hg., s.f.=1.02, and for a 2 micron drop, s.f.=1.04. Since the percentage error in Δs was largest for the drop sizes for which the "slip factor" would begin to be important, it was not expected that neglecting this factor would change the results to any appreciable degree.

Several other possibilities were investigated. A change in the humidity of the air in the drift tube during the course of a data run could have produced a difference in the rate of evaporation between the beginning and end of the run.

An examination of the data did not reveal time dependent trends.

Another possibility was the existance of convection currents within the drift tube. The data would seem to indicate that this was not a problem. If the convection current was steady, it would not have produced the scatter in $d(a^2)/dt$ at a given dew point depression. On the other hand, if it were turbulent, this would have produced a greater scatter of points around the Δs-t line for individual drops. Also, the drops were observed while they were falling, and no effects of convection currents were noted.

A further possibility involves the drops themselves. It has been assumed that the drops were pure water. Since they were formed in a diffusion cloud chamber on condensation nuclei, they were, in fact, contaminated to varying degress. It is known that comtaminants lower the vapor pressure over the liquid surface and can have an effect on the rate of evaporation. Unfortunately, the size and properties of the nuclei are unknown. It is believed that this effect was minimal, as the filter that was used should have removed most of the larger nuclei.

The second discrepancy in Figs. 5-7 are the non-zero values for the dew point depression at zero rates of evaporation. These are equal to or greater than the estimated error in the temperature measurements. The reason for this may be explained by the fact that these are values extrapolated from a curve that was fitted to scattered data.

A possible experimental source of error concerns the humidifying method. Although the water in the humidifier was changed prior to each run, there was still the possibility that it could become contaminated. This would lower the vapor pressure and give a dew point temperature lower than that indicated by the temperature of the bath.

DISCUSSION AND CONCLUSIONS

The experimental results have been compared with the ate of evaporation calculated from the quasistationary heory and the formulations given by Kinzer and Gunn (1951) nd Squires (1952). These comparisons are shown in Table III nd for T_A=30C in Fig. 10.

In the following discussion the temperature lowering of he drop due to evaporation has been included in the uasistationary theory (see Eqs. 12-14). Since the dew point epression was less than 0.6C one can use to a good pproximation a linear relationship between the water vapor ensity and temperature (ρ_v=bT+C) rather than the Clausius-lapeyron equation. (The numerical values of b and C can be alculated from a table of vapor density versus temperature, nd for b are listed in Appendix II.) Substituting this pproximation into Eq. 12 and eliminating ρ_a and T_a gives:

$$\frac{d(a^2)}{dt} = \frac{2D}{\rho_\ell}\left(\frac{\Gamma}{\Gamma+b}\right)\{\rho_\infty - (bT_\infty+C)\} \quad , \tag{41}$$

here ρ_∞ and T_∞ are measurable quantities. Similarly, as the umidity was characterized by the dew point depression, it as convenient to express ρ_∞ in terms of the dew point emperature, i.e. ρ_∞=bT_{dp}+C, where b and C are numerically he same as above. The rate of evaporation is then given by:

TABLE III

Comparison of experimentally determined and theoretical rates of evaporation

*Slopes of lines $d(a^2)/dt=B\Delta T$

TEMPERATURE	EXPERIMENTAL	UPPER BOUND	LOWER BOUND	QUASI.(1)	QUASI.(2)	KINZER & GUNN	SQUIRES
25C	16.61	17.33	15.88	15.87	16.46	20.78	15.53
30C	19.11	19.88	18.34	17.10	17.78	23.81	16.85
35C (75)	19.22	20.75	17.68	18.24	19.00	26.65	18.04
35C (67)	20.29	21.45	19.14	18.24	19.00	26.65	18.04

*Units of slope: $\frac{\text{micron}^2}{\text{sec-}^{o}\text{C}}$

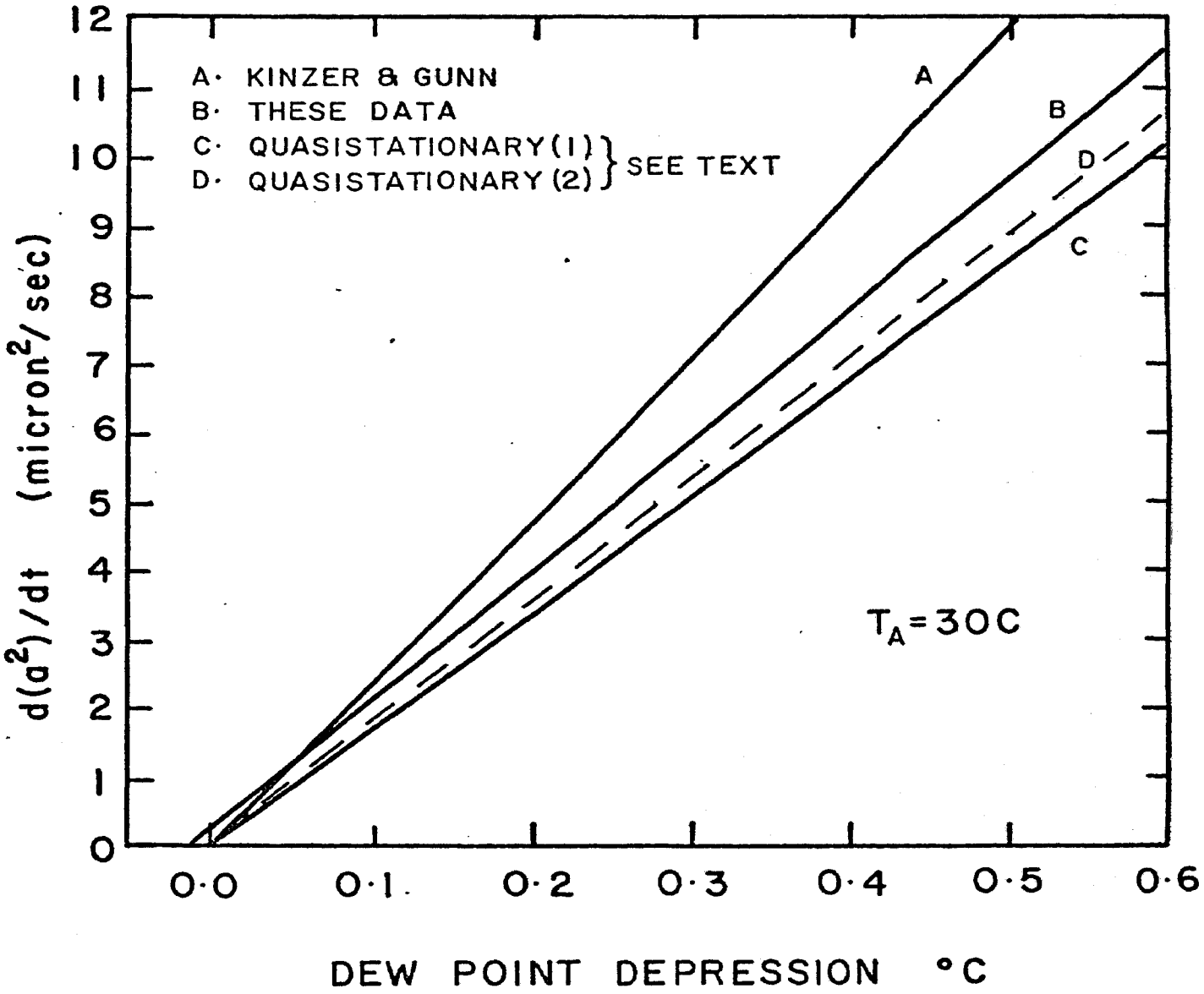

Fig. 10. A comparison of experimental and theoretical evaporation rates at 30C.

$$\frac{d(a^2)}{dt} = \frac{2D}{\rho_\ell}\left(\frac{\Gamma \cdot b}{\Gamma + b}\right)(T_{dp} - T_\infty) \quad , \tag{42}$$

here $T_{dp}-T_\infty$ is the dew point depression. The values for the iffusion coefficient, D; the thermal conductivity, κ; and he latent heat of vaporization, L, are listed in Appendix II. he diffusion coefficients were obtained by averaging the alues given by Reid and Sherwood (1958) and Fuller, et al 1966).

The values for the thermal conductivity of air were btained from the work of Taylor and Johnston (1946). The ates of evaporation which were calculated using these values re noted as *quasistationary* (1) in Table III and Fig. 10. t seems, however, that there are serious questions concer- ng the correct values for κ. The latest measured values Saksena and Saxena, 1966) are numerically larger than those f Taylor and Johnston, the differences becoming greater at ower temperatures. At the lower limit of the temperature ange over which κ was measured, 40C, the value of κ was -6% greater than that of Taylor and Johnston. Because of his discrepancy, the rates of evaporation were also alculated using values of κ 5% greater than used previously. he resultant rates are noted by *quasistationary* (2) in able III and Fig. 10.

The rate of evaporation as given by Kinzer and Gunn 1959) reduces to

$$\frac{d(a^2)}{dt} = \frac{2D}{\rho_\ell}(\rho_{wb}-\rho_\infty) \qquad (43)$$

or small Re, where ρ_{wb} is the saturation vapor density at ie temperature of the ventilated wet bulb. Using the same pproximation for the relationship between vapor density nd temperature as before, the rate may also be written as:

$$\frac{d(a^2)}{dt} = \frac{2Db}{\rho_\ell}(T_{wb}-T_{dp}) \ . \qquad (44)$$

n order to compare this with the experimental results, it as necessary to calculate the dew point corresponding to a iven wet bulb temperature. Using Eq. 44 the rate of vaporation was calculated. As with the experimental results, he calculated rates were plotted versus dew point depression. he slope, β, of the line, $d(a^2)/dt|_{K\&G} = \beta\Delta T$, was determined, here ΔT is the dew point depression. This was done by etermining the relative humidity at the given wet bulb emperature, using the psychrometric equation for a ventilated et bulb given by the U.S. Weather Bureau. Once the relative umidity was known, the corresponding vapor density was etermined from which the dew point and dew point depression ere calculated.

The rate of evaporation as given by Squires was alculated in full for a freely falling 5 micron drop, e=0.06. The calculation is tedious but straight forward. he values of the water vapor pressure used are listed in

endix II, while the other physical constants are the same noted before.

Referring to Table III, it is noted that the rates of poration given by Squires are quite close to those given the quasistationary theory, Quasi. (1), and for this ison have not been plotted in Fig. 10.

The rates determined from Kinzer and Gunn's formulation in all cases much higher than the experimental results. s is probably due to the use of the ventilated wet bulb perature, even though it was implied that there was no tilation, i.e. the ventilation factor was zero.

To compare the experimental results with theory, it is e convenient to note the differences in the slopes, β, of lines $d(a^2)/dt = \beta\Delta T + R_o$ rather than the individual rates a specific dew point depression. In the following scussion, the non-zero intercepts of the experimental sults have been ignored. If the data were corrected for ts, it would cause a shift only in the y-axis, and would affect the slopes or make the data fit the theory any tter.

For all temperatures, the experimental results are gher than the rates given by the quasistationary theory. some cases, however, the confidence limits of the perimental results include the rates given by the asistationary theory, which is not true in the comparison th Kinzer and Gunn. The lower bound for the data at 25C is most identical with the rate given by Quasi. (1). The rate

35C (75), where (75) is the number of drops involved, has ɔwer bound that includes the quasistationary rate. ıough the experimental results at 35C (75) agree better ı the results at other temperatures, the group of data at 35C, $\Delta T=0.28C$, is viewed with suspicion. The slope, noted 35C (67), calculated with this group of data excluded ears to be more in line with the data at the other ɔeratures, but does not include the Quasi. (1) slope hin its lower bound.

Comparing the experimental results to the sistationary rates in which the thermal conductivity of air has been increased 5%, Quasi. (2), it is noted that le the experimental results are still high, the agreement ɔetter. The lower confidence limits at 25C and 35C (75) lude the Quasi. (2) rate, and at 35C (67) the limit is t above this rate.

There are two possible reasons for the experimental ılts being higher than is predicted by the quasistationary ɔry. The first concerns the validity of the values of κ ı. If the data of Saksena and Saxena had been rapolated to the temperature range of present interest, ir values would have been as much as 10% higher than lor and Johnston's. The quasistationary rates determined ıg a 10% increase in κ give slopes of 17.04, 18.45 and 74 at 25C, 30C and 35C respectively which place these es all within the confidence limits of the experimental ılts. The other possibility is a ventilation effect.

:ver, this was included in the calculation using Squires'
ıulation, and the rates obtained were less than those
:n by the quasistationary theory. The experimental results,
:aused by ventilation, indicate that the ventilation
:ct is greater than predicted by Squires, but not to the
:nt that the drop would take on the temperature of a
:ilated wet bulb as implied by Kinzer and Gunn.

One final possibility that should be mentioned concerns
validity of the diffusion theory in general. It has been
ımed in the development of the theory that the drop was
porating into a uniform gas that was not affected by
rmal expansion. In reality, this is not the case. Gases
e a large thermal expansion coefficient, and with the
t flow that is involved, the gas surrounding an
porating drop is very much non-uniform. Whether the error
to assuming a uniform gas is sufficient enough to explain
difference between the experimental results and the
ory remains to be seen.

APPENDIX I

LIST OF SYMBOLS

a drop radius

b constant defined by $\rho_v = bT + C$

b' slope of experimentally determined evaporation rate curve

c vapor concentration

c_∞ vapor concentration at a distance removed from the drop

c_s vapor concentration at drop surface

C constant defined by $\rho_v = bT + C$

D diffusion coefficient

f ventilation factor

$f(Re)^{\frac{1}{2}}$ a function of $(Re)^{\frac{1}{2}}$ (see Kinzer and Gunn, 1951)

g acceleration due to gravity

I rate of diffusion

M $4\pi aD(c_s - c_\infty)$, Maxwell's evaporation rate

k Boltzmann's constant

s $\frac{9\eta}{2(\rho_\ell - \rho_A)g}$

L latent heat of vaporization

m mass of drop

m' molecular weight of evaporating substance

u Nusselt number

p vapor pressure

p_A atmospheric pressure

r Prandtl number

r distance from center of drop; radial coordinate

R gas constant

Re	Reynolds number
R_o	Experimental rate of evaporation at $\Delta T=0$
s	distance drop fell in 0.5 sec
Sc	Schmidt number
Sh	Sherwood number
t	time
T	temperature
T_a	temperature of drop surface
T_A T_∞	temperature of surrounding medium, at a distance removed from the drop
T_{dp}	dew point temperature
T_{wb}	temperature of a ventilated wet bulb
ΔT	dew point depression
V	velocity of air stream with respect to drop at a distance removed from the drop
α	evaporation-condensation coefficient
Γ	κ/DL
ε	specific gravity of water vapor with respect to dry air
η	viscosity of air
κ	thermal conductivity of air
λ	mean free path of air molecules
ν	kinematic viscosity
ρ_A	density of air
ρ_{dp}	saturated vapor density at dew point
ρ_∞	vapor density in surrounding medium at a distance removed from the drop
ρ_ℓ	density of the drop

ρ_s saturated vapor density at drop surface
ρ_a

ρ_{wb} saturated vapor density at the temperature of a ventilated wet bulb

σ surface tension

APPENDIX II

PHYSICAL CONSTANTS

PROPERTY	VALUE AT TEMPERATURE 25C	30C	35C		SOURCE
Viscosity of air	183.2	185.6	188.0	μ poise	ICT
Density of air	1.124	1.101	1.077	gm/liter	Hodgman
Thermal conductivity of air	6.067×10^{-5}	6.148×10^{-5}	6.229×10^{-5}	$\frac{\text{cal}}{\text{sec-cm-}^{o}\text{K}}$	Taylor and Johnston
Density of water	0.997	0.996	0.994	gm/cc	Hodgman
$K_s = \frac{9\eta}{2(\rho_\ell - \rho_A)g}$	8.446	8.569	8.694	$\frac{\text{micron}^2\text{-sec}}{\text{mm}}$	Calculated from Stokes' Law
Diffusion coefficient	0.261	0.270	0.278	cm^2/sec	Reid and Sherwood, and Fuller, et.al.
Coefficient of T from $\rho_v = bT + C$	1.26×10^{-6}	1.60×10^{-6}	2.03×10^{-6}	$\frac{\text{gm}}{\text{cc-}^{o}\text{K}}$	Hodgman
Heat of vaporization of water	582.8	579.5	576.8	cal/gm	ICT
Atmospheric pressure	730	-----	-----	mm Hg	Measured
Water vapor pressure	23.76	31.82	42.18	mm Hg	Hodgman

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